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Porphotetramethenes with 1,3-alternate conformation of pyrrole rings from oxidative *N*-alkylation of porphyrin tetraphenols

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Abstract—Tetrapyrrole macrocycles, of which the pyrroles are connected by sp² centers, were readily obtained from porphyrin tetraphenols by air oxidation under basic conditions, followed by *N*-alkylation. The degree of *N*-alkylation could be controlled and either di- or tetraalkylated derivatives are obtained in high yields. © 2003 Elsevier Science Ltd. All rights reserved.

In earlier work,¹ we described porphyrin dendrimers with tetraphenol **1** as the core. However, it was not possible to prepare dendrimers having porphyrin groups at several tiers of the structure due to the poor solubility of compound **1**.² Therefore, we wanted to study the use of **2** as a soluble porphyrin core reagent. Thus, **2** was reacted with the first generation Fréchet dendron under the standard conditions (K₂CO₃, acetone, reflux). It became immediately clear that, we did not obtain the expected porphyrin but a good yield of a red product **3a** resulting from oxidation of **2** and tetraalkylation of the pyrrole nitrogens. In a series of articles, Milgrom³ studied the multistep oxidation of phenol derivatives of porphyrin **2** and related compounds. Via a number of stable radicals, the porphodimethene **4** was obtained as apparent from NMR measurements.^{3a} In the solid form however, the structure of the oxidized product is described by X-ray crystallography as a porphotetramethene

of structure similar to **3a**.^{3b} We can assume that this compound **4** is the intermediate before the alkylation. We decided to study in detail these oxidative alkylation reactions of **2** leading to tetraalkylated derivatives **3**. Earlier alkylation experiments of isolated **3c** in refluxing basified DMF gave only low yields of tetraalkylated porphotetramethenes **3**, but mainly partly alkylated compounds (Figs. 1 and 2).

Benzylation of **2** under the same conditions as for the formation of **3a** (acetone, K₂CO₃, reflux) gave the (red) tetraalkylated compound **3b**.^{3c} In principle, four different isomers could form, which we can name, in analogy with calix[4]arene nomenclature, the ‘cone’, ‘partial cone’, ‘1,2-alternate’ and ‘1,3-alternate’ form.⁴ The ¹H NMR spectrum of **3b** showed that all pyrrole hydrogens were equivalent, which does not agree with the symmetry of partial cone or 1,2-alternate isomers. Obviously, the cone isomer would be very hindered. The related calix[4]pyrroles⁵ have a similar 1,3-alternate structure when not complexed.⁶ An X-ray crystallographic study showed clearly that the 1,3-alternate tetraalkylated isomer belonged to point group *S*₄. (Fig. 3) The benzene substituent and pyrrole ring make an angle of 84.9° (**2**) with each other. The asymmetric unit consists of a quarter of the molecule and a toluene molecule (crystallization solvent). There is no hydrogen network as described by Milgrom,^{3b} but the unit cell contained four voids of 583 Å³ each, which are surrounded by *t*-butyl groups and possibly contain more disordered solvent molecules.

Because of the similarity of the UV and NMR spectra, we can assign the 1,3-alternate structure **3a** to the product by analogy to **3b**.

Upon treatment of **2** in acetone with sodium hydride as the

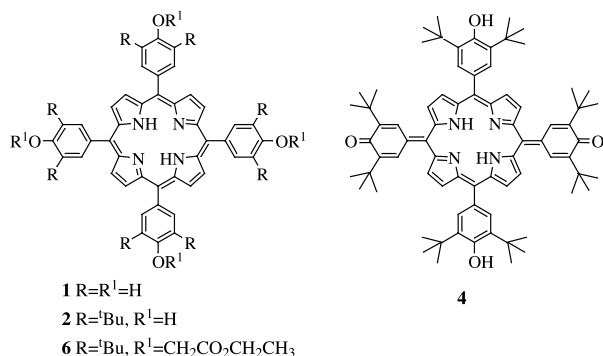


Figure 1. Structures of compounds **1**, **2**, **4** and **6**.

Keywords: alkylation; *meso*-tetrakis; porphotetramethenes.

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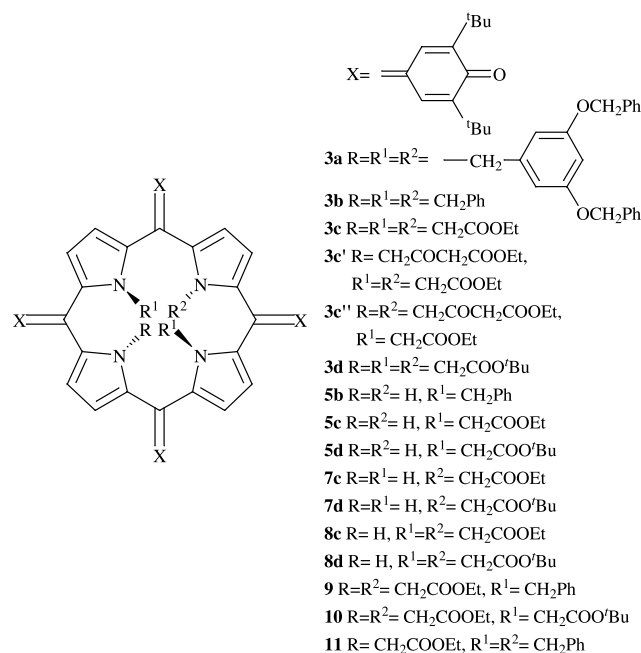


Figure 2. Structures of **3a–d**, **5b–d**, **7c–d**, **8c–d**, **9**, **10**, **11**.

base, an immediate and quantitative transformation of the tetraphenolate to the porphodimethene **4** takes place after air oxidation. The addition of benzyl bromide to the reaction mixture resulted in the formation of a purple compound, and the latter could be isolated in 81% yield by quenching of the reaction mixture after 30 min, together with some tetraalkylated compound **3b**. Longer reaction times only gave **3b** (see Table 1). The intermediate compound was assigned by 1H NMR the *N*-dialkylated porphodimethene structure **5b**, having benzyl groups on alternating pyrrole rings. We can assume that the two benzyl substituents are on the same side of the macrocycle since they appear like this in the final product. We would like to stress that the yields

are significantly higher than those reported by Milgrom^{3c} (81% instead of 32% for **5b**, and 86% instead of 3% for **3b**). Mono- and tribenzylated intermediate products were not obtained.

Other alkylating agents, such as ethyl iodide did not yield products similar to **3b** and **5b** using our experimental conditions. However, addition of excess of the reactive ethyl bromoacetate to solutions of **2** in the presence of a base gave reaction mixtures containing several alkylated products. However, the reaction was slower than the benzylation reaction. The composition of the reaction mixtures depends on the used conditions (solvent, base, time, Table 1). Reaction with potassium carbonate in refluxing acetone gave a very complex mixture from which, together with the *N*-tetraalkylated product **3c**, an *O*-tetraalkylated porphyrin **6** could be isolated. Mass spectral analyses of other fractions showed that several partially *O*-alkylated compounds were present. Also, some starting material **2** was recovered. With the weaker base potassium carbonate, no tetraphenolate derived from **2** was formed, and the oxidation to **4** did not proceed previous to the alkylation. Therefore, in all subsequent experiments we decided to use stronger bases, such as sodium hydride and potassium *t*-butoxide, which led to complete oxidation of **2** to **4** prior to alkylation. In this case no *O*-alkylation occurred and monoalkylated, dialkylated, trialkylated and tetraalkylated tetrapyrroles were obtained depending on the reaction conditions (Table 1). Partially alkylated products **5c** and **7c** could be isolated and treated with excess ethyl bromoacetate and base to give tetraalkylated product **3c**. In some cases, and especially when DMSO is the solvent, the tetraalkylated compound **3c** contained some trialkylated derivative **8c**, which could not be separated by chromatography. In other cases, hydrolysis of excess of ethyl bromoacetate occurred under the reaction conditions and the ethyl 2-hydroxyacetate induced transesterification of **3c**, forming products **3c'** and **3c''** which could be separated with some difficulty from **3c**. However, treatment with excess of ethoxide reconverts the mixture **3c**/**3c'**/**3c''** completely to **3c**. Alkylation of **2** with the sterically hindered *t*-butyl bromoacetate gave similar mixtures of monoalkylated **7d**, dialkylated **5d**, trialkylated **8d**, and tetraalkylated **3d** without transesterification (see Table 1).

The dialkylated product **5c** could be obtained in good yield (60%, Table 1, entry 21), and was benzylation to give a tetraalkylated compound **9** having two different alkyl groups. Alternatively, the dialkylated porphodimethene **5b** could be reacted with ethyl bromoacetate and base to afford the identical compound **9**. Therefore, we have to assume structural analogy between the dialkylated compounds **5b** and **5c**. Moreover, alkylation of **5c** with *t*-butyl bromoacetate gave a tetraalkylated derivative **10**, with the alternating ester groups selectively protected. The isolated monoacetate **7c** could be smoothly tribenzylated with base and benzyl bromide to the product **11**. Each of these products **3–7** and **9–11** was isolated by column chromatography and completely characterized by 1H and ^{13}C NMR spectroscopy, electrospray mass spectra and UV spectroscopy.

Further work in our laboratories was carried out in order to use these *N*-alkylation reactions for the construction of

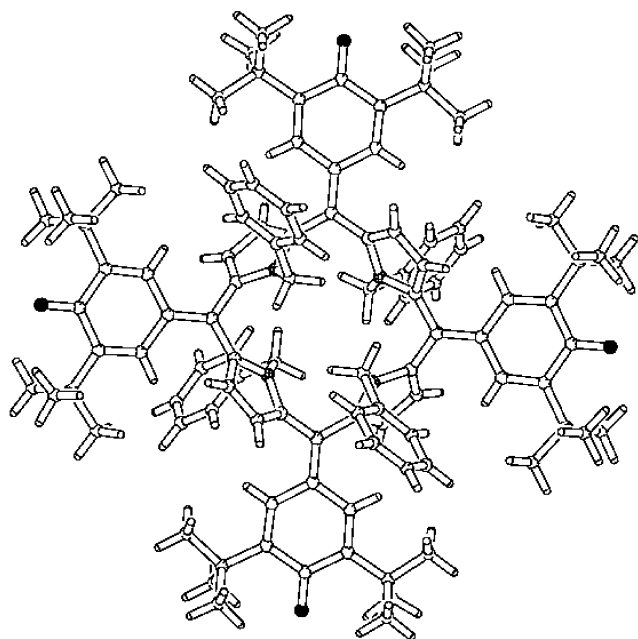


Figure 3. Molecular structure of **3b**. Toluene has been omitted for clarity.

Table 1. Yields and products for the N-alkylation reactions

Starting compound	Solvent	Alkylating agent	Temperature (°C)	Reaction time	Total yield (%)	% of total yield			
						Mono	Di	Tri	Tetra
2	DMF	BrCH ₂ CO ₂ Et	56	15 h	21	43	21	0	36 ^a
2		BrCH ₂ CO ₂ Et	82	15 h	36	37	21	0	42 ^a
2		BrCH ₂ CO ₂ Bu	82	15 h	26	3	10	0	87
2		BrCH ₂ CO ₂ Et	100	15 h	83	1	23	0	76 ^a
2		BrCH ₂ CO ₂ Bu	100	15 h	41	10	ni ^b	0	90
2	CH ₃ CN	BrCH ₂ CO ₂ Et	56	15 h	40	5	31	0	64
2		BrCH ₂ CO ₂ Bu	56	15 h	23	0	0	0	100
2		BrCH ₂ CO ₂ Et	82	15 h	40	6	28	0	66
2		BrCH ₂ CO ₂ Bu	82	15 h	43	0	0	0	100
2		BrCH ₂ CO ₂ Et	56	15 h	100	18	29	0	53
2	THF ^c	BrCH ₂ CO ₂ Bu	56	15 h	100	10	48	4	38
2		BrCH ₂ CO ₂ Et	82	15 h	23	33	12	35	20
2		BrCH ₂ CO ₂ Bu	82	15 h	91	5	12	5	78
2		BrCH ₂ CO ₂ Et	100	15 h	30	28	15	34	23
2		BrCH ₂ CO ₂ Bu	100	15 h	70	3	8	3	86
2	DMSO	BrCH ₂ CO ₂ Et	56	30 min	98	0	82	0	18
2		BrCH ₂ CO ₂ Et	56	6 h	86	0	0	0	100
2		BrCH ₂ CO ₂ Et	56	15 h	63	0	0	0	100
5c		BrCH ₂ CO ₂ Et	56	5 days ^d	86	0	0	0	100 ^e
5b		BrCH ₂ CO ₂ Et	56	15 h	75	0	0	0	100
2	acetone	BrCH ₂ CO ₂ Et	56	45 min ^f	82 ^g	0	73	0	27
7c		BrCH ₂ CO ₂ Et	56	6 h	55	0	0	0	100
5c		BrCH ₂ CO ₂ Bu	56	4 h	90	0	0	0	100
2		BrCH ₂ CO ₂ Bu	56	1 h ^h	45	30	70	0	ni ^b
2		BrCH ₂ CO ₂ Bu	rt	15 h	100	ni ^b	21	ni ^b	79
2		BrCH ₂ CO ₂ Et	56	15 h	72	9	43	0	48
2		BrCH ₂ CO ₂ Bu	56	15 h	99 ⁱ	ni ^b	17	ni ^b	83

^a The tetraalkylated product contained 12–20% **3c'**.^b Not isolated, traces present (TLC).^c *t*BuOK was used as base as we saw no conversion with NaH.^d 80 equiv. of NaH, 105 equiv. of the bromoester.^e The tetraalkylated product contained 26% **3c'** and 29% **3c''**.^f 13 equiv. of the bromoester.^g The method of choice (60%) for **5c**.^h 8 equiv. of the bromoester, 2.5 times diluted.ⁱ The method of choice (82%) for **3d**.

strapped derivatives of the porphotetramethenes **3** and their use as host compounds.

1. Experimental

The ¹H NMR and ¹³C NMR data in CDCl₃ solution at 30°C were recorded on a Bruker AMX 400 MHz spectrometer. The chemical shifts are reported in ppm relative to TMS as an internal standard. *J* values are given in Hz. The UV/Vis data are given as λ_{max}/nm in CH₂Cl₂. The MS data were obtained on a Micromass Quattro II mass spectrometer in ESI (infusion of 50 μl MeOH/CH₂Cl₂–NH₄OAc (0.1 M in MeOH) with a Harvard pump, model 11). Column chromatographies were performed on silica gel (63–200 mesh) eluting with dichloromethane. TLC inspections on silica gel F₂₅₄ plates were performed with dichloromethane. *Meso*-tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)porphyrin **2** was prepared by a literature procedure.^{3a} All other reagents and solvents were commercially available and used as purchased. All compounds do not melt below 300°C so no mps are included.

1.1. General conditions for the reactions reported in Table 1

0.18 mmol (200 mg) of the starting porphyrin **2** (or an

equivalent amount of compounds **5** or **7**) and 60–65 mg NaH (80 wt% in mineral oil, ~10 equiv.) were stirred in 20 ml solvent at room temperature for 10–15 min. Then 4.43 mmol (25 equiv.) of the alkylating agent (787 mg of BrCH₂CO₂Et, 873 mg of BrCH₂CO₂Bu, 769 mg of BrCH₂C₆H₅) in 5 ml solvent was added and the reaction mixture heated (oil bath) to the indicated temperature. After the reaction time indicated in the table, the reaction mixture was cooled, taken into CH₂Cl₂, the solution washed three times with water, dried over MgSO₄, and evaporated to dryness. The mixture of products was then isolated by column chromatography on silica with CH₂Cl₂ as the eluent. The ratios of the products were estimated by the integrals of their signals in the ¹H NMR spectra (300 MHz, CDCl₃) of the product mixtures. The products could be further separated from the mixtures by careful column or plate chromatography. For the reactions in THF, KO^{*t*}Bu (465 mg) was used instead of NaH and the synthetic procedure carried out in the same way.

1.1.1. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclo-hexa-2,5-dienylene)-N₂₁,N₂₂,N₂₃,N₂₄-tetra(3,5-di(benzyloxy)benzyl)porphyrinogen **3a.** A mixture of 500 mg (0.44 mmol) **2**, 561 mg 3,5-di(benzyloxy)benzyl bromide (1.46 mmol), 202 mg K₂CO₃ (1.46 mmol) and 12 mg 18-crown-6 (0.04 mmol) in 15 ml acetone was refluxed for 4 h. Upon cooling, the mixture was taken into

30 ml CH_2Cl_2 and washed three times with 30 ml water, dried over MgSO_4 , and evaporated to dryness. Column chromatography on silica with CH_2Cl_2 /hexane (3:1) as the eluent afforded the title compound in 60% yield (623 mg). δ_{H} 7.24–7.30 (m, 48H), 6.52 (s, 8H, pyrrole H), 6.39 (t, $J=2.0$ Hz, 4H), 5.85 (d, $J=2.0$ Hz, 8H), 4.79 (s, 16H), 4.28 (s, 8H), 1.19 (s, 72H, *t*-butyl); δ_{C} 186.0 (quinoid C=O), 160.1 (3- and 5-C of the trisubstituted benzyl), 148.2 (3-quinoid), 139.5 (1-C of the trisubstituted benzyl), 138.1 (pyrrole α -C), 136.2 (1-C of the phenyl), 133.8 (1-quinoid), 131.5 (2-quinoid), 130.7 (*meso* C), 128.6 (3- and 5-C of the phenyl), 128.1 (4-C of the phenyl), 127.5 (2- and 6-C of the phenyl), 120.8 (pyrrole β -C), 105.9 (2 and 6-C of the trisubstituted benzyl), 100.4 (4-C of the trisubstituted benzyl), 70.1 (CH_2 of the monosubstituted benzyl), 48.6 (NCH_2Ar), 35.4 (*t*-butyl quaternary C), 29.3 (*t*-butyl CH_3); ESI-MS 2336 (MH^+).

1.1.2. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclo-hexa-2,5-dienylene)- $N_{21},N_{22},N_{23},N_{24}$ -tetrabenzylporphyrinogen **3b.** *Method A*: a mixture of 500 mg (0.44 mmol) **2**, 344 mg benzyl bromide (1.95 mmol), 270 mg K_2CO_3 (1.95 mmol) and 12 mg 18-crown-6 (0.04 mmol) in 15 ml acetone was refluxed under argon for 12 h. Upon cooling, the mixture was taken into 30 ml CH_2Cl_2 and washed three times with 30 ml water, dried over MgSO_4 , and evaporated to dryness. Column chromatography on silica with CH_2Cl_2 /hexane (3:1) as the eluent afforded the title compound in 60% yield (400 mg). *Method B*: a mixture of 100 mg (0.09 mmol) **2**, 25 mg NaH (0.83 mmol) and 390 mg (2.28 mmol) benzyl bromide in 15 ml acetone was reacted in the usual way for 6 h. The crude product was purified by recrystallization from CH_2Cl_2 /methanol to afford the title compound in 86% yield (115 mg). The spectral data were identical to the ones found in the literature;^{3c} UV/Vis 330.6, 504.4; ESI-MS 1487 (MH^+). The compound was recrystallized from toluene for X-ray analysis: ($\text{C}_{104}\text{H}_{116}\text{N}_4\text{O}_4 \cdot 4(\text{C}_7\text{H}_8)$): crystal dimensions $0.45 \times 0.45 \times 0.20 \text{ mm}^3$, tetragonal, $I4_1/a$, $a=30.797(4)$, $c=13.317(3) \text{ \AA}$, $V=12631(4) \text{ \AA}^3$, $Z=4$, $\rho_{\text{calcd}}=0.975 \text{ g cm}^{-3}$, $2\theta_{\text{max}}=46.6^\circ$, $\mu(\text{Mo K}\alpha)=0.058 \text{ cm}^{-1}$, MAR345 imaging plate detector, Mo $\text{K}\alpha$ ($\lambda=0.71073 \text{ \AA}$), graphite monochromated, $T=100 \text{ K}$, 16389 measured reflections, 4534 independent reflections. The data were corrected for Lorentz and polarization effects. Structure solved by direct methods, full-matrix least-squares refinement based on $|F|^2$, 324 parameters, hydrogen atoms placed at calculated positions and refined in riding mode with temperature factors 20% higher than parent atom (50% for methyl groups), $R1=0.0814$ (for 3617 data with $I>2\sigma(I)$), $wR2=0.2447$, max/min residual electron density $0.47/-0.21 \text{ e}^- \text{ \AA}^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-170961. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

1.1.3. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclo-hexa-2,5-dienylene)-porphyrinogen **4.** 0.05 mmol (51 mg) of the porphyrin **2** and 11 mg (8 equiv.) NaH were stirred in 5 ml acetone for 15 min. The reaction

mixture was taken into CH_2Cl_2 and the solution washed with water, dried over MgSO_4 , and evaporated to dryness. Recrystallization from CH_2Cl_2 /light petroleum ether afforded the title compound in 79% yield (40 mg).^{3a}

1.1.4. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- N_{21},N_{23} -dibenzylporphyrinogen **5b.** A mixture of 100 mg (0.09 mmol) **2**, 25 mg NaH (0.83 mmol) and 390 mg (2.28 mmol) benzyl bromide in 15 ml acetone was reacted for 30 min in the usual way. The reaction mixture was taken into CH_2Cl_2 and the solution washed with water, dried over MgSO_4 , and evaporated to dryness. After column chromatography in CH_2Cl_2 on silica the title compound was isolated in 81% overall yield (95 mg), along with some **3b** (Table 1).^{3c}

1.1.5. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-ethoxy-carbonyl)methoxy)-porphyrin **6.** A mixture of 475 mg (0.42 mmol) of the porphyrin **2**, 450 mg (2.61 mmol) $\text{BrCH}_2\text{CO}_2\text{Et}$ and 500 mg (3.61 mmol) K_2CO_3 in 20 ml acetone was refluxed for 6 days. Further aliquots of $\text{BrCH}_2\text{CO}_2\text{Et}$ were added at irregular time intervals up to a total of 2.22 g (12.89 mmol). The reaction mixture was cooled, taken into 70 ml CH_2Cl_2 , washed three times with water and dried over Na_2SO_4 . Repeated column chromatography in CH_2Cl_2 /hexane mixtures on silica afforded 103 mg (17%) of **6** along with a mixture of partially O-alkylated compounds (which were not isolated, but their presence was determined by MS) and 108 mg (17%) **3c**. δ_{H} 8.90 (br s, 8H, pyrrole H), 8.14 (s, 8H, phenyl H), 4.71 (s, 8H, OCH_2CO_2), 4.42 (q, $J=7.2$ Hz, 8H, ethyl CH_2), 1.61 (s, 72H, *t*-butyl), 1.42 (t, $J=7.2$ Hz, 12H, ethyl CH_3), -2.69 (s, 2H, inner NH); δ_{C} 168.7 (COO), 156.0 (4-phenyl), 141.6 (3-phenyl), 137.3 (1-phenyl), 131.1 (pyrrole β -C), 133.8 (2-phenyl), 120.5 (*meso* C), 73.3 (OCH_2CO_2), 61.2 (ethyl CH_2), 36.1 (*t*-butyl quaternary C), 32.4 (*t*-butyl CH_3), 14.3 (ethyl CH_3); UV/Vis 422.3, 519.0, 555.5, 593.5, 649.4; ESI-MS 1472 (MH^+).

1.2. Analytical data for the compounds reported in Table 1 and prepared according to the general conditions above

1.2.1. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- $N_{21},N_{22},N_{23},N_{24}$ -tetra((ethoxy-carbonyl)methyl)porphyrinogen **3c.** δ_{H} 7.47 (s, 8H, quinoid H), 6.64 (s, 8H, pyrrole H), 4.00 (q, $J=7.1$ Hz, 8H, ethyl CH_2), 3.83 (s, 8H, NCH_2CO_2), 1.31 (s, 72H, *t*-butyl), 1.08 (t, $J=7.1$ Hz, 12H, ethyl CH_3); δ_{C} 186.2 (quinoid C=O), 167.1 (COO), 148.4 (3-quinoid), 138.7 (pyrrole α -C), 135.2 (1-quinoid), 131.3 (2-quinoid), 128.8 (*meso* C), 120.1 (pyrrole β -C), 61.9 (ethyl CH_2), 46.3 (NCH_2CO_2), 35.5 (*t*-butyl quaternary C), 29.4 (*t*-butyl CH_3), 14.2 (ethyl CH_3); UV/Vis 323.8, 495.5; ESI-MS 1470 (MH^+).

1.2.2. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- $N_{21},N_{22},N_{23},N_{24}$ -tetra(*t*-butoxy-carbonyl)methyl)porphyrinogen **3d.** δ_{H} 7.52 (s, 8H, quinoid H), 6.64 (s, 8H, pyrrole H), 3.70 (s, 8H, NCH_2CO_2), 1.32 (s, 72H, ring *t*-butyl), 1.26 (s, 36H, $\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$); δ_{C} 186.3 (quinoid C=O), 166.3 (CO₂), 148.2 (3-quinoid), 138.7 (pyrrole α -C), 135.0 (1-quinoid),

131.6 (2-quinoid), 129.3 (*meso* C), 119.9 (pyrrole β -C), 82.7 ($\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$), 47.2 (NCH_2Ar), 35.5 (ring *t*-butyl quaternary C), 29.4 (ring *t*-butyl CH_3), 28.0 ($\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$); UV/Vis 325.2, 498.1; ESI-MS 1582 (MH^+).

1.2.3. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- N_{21},N_{23} -di((ethoxycarbonyl)methyl)porphyrinogen 5c. δ_{H} 9.26 (br s, 2H, NH), 7.58 (d, $J=2.5$ Hz, 4H, quinoid H), 7.35 (d, $J=2.5$ Hz, 4H, quinoid H), 6.83 (d, $J=2.3$ Hz, 4H, pyrrole bearing NH), 6.56 (s, 4H, pyrrole bearing NR), 3.99 (q, $J=7.1$ Hz, 4H, ethyl CH_2), 3.91 (s, 4H, NCH_2CO_2), 1.34 (s, 36H, *t*-butyl), 1.29 (s, 36H, *t*-butyl), 1.05 (t, $J=7.1$ Hz, 6H, ethyl CH_3); δ_{C} 186.2 (quinoid C=O), 167.1 (COO), 148.5, 147.6 (3-quinoid), 137.6 (pyrrole (bearing NR) α -C), 134.9 (pyrrole (bearing NH) α -C), 133.2 (1-quinoid), 132.0, 130.6 (2-quinoid), 129.8 (*meso* C), 119.5, 118.8 (pyrrole β -C), 62.1 (ethyl CH_2), 46.5 (NCH_2CO_2), 35.6, 35.4 (*t*-butyl quaternary C), 29.6, 29.5 (*t*-butyl CH_3), 14.0 (ethyl CH_3); UV/Vis 327.9, 502.8; ESI-MS 1298 (MH^+).

1.2.4. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- N_{21},N_{23} -di(*t*-butoxycarbonyl)methylporphyrinogen 5d. δ_{H} 9.27 (br s, 2H, NH), 7.60 (d, $J=2.3$ Hz, 4H, quinoid H), 7.37 (d, $J=2.3$ Hz, 4H, quinoid H), 6.83 (d, $J=2.2$ Hz, 4H, pyrrole bearing NH), 6.54 (s, 4H, pyrrole bearing NR), 3.78 (s, 4H, NCH_2CO_2), 1.35 (s, 36H, ring *t*-butyl), 1.29 (s, 36H, ring *t*-butyl), 1.22 (s, 18H, $\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$); δ_{C} 186.2 (quinoid C=O), 166.3 (COO), 148.5, 147.5 (3-quinoid), 137.7 (pyrrole (bearing NR) α -C), 135.0 (pyrrole (bearing NH) α -C), 133.2 (1-quinoid), 132.4, 130.6 (2-quinoid), 130.1 (*meso* C), 119.4, 118.4 (pyrrole β -C), 83.1 ($\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$), 47.5 (NCH_2Ar), 35.6, 35.4 (*t*-butyl quaternary C), 29.6, 29.5 (ring *t*-butyl CH_3), 27.9 ($\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$); UV/Vis 328.0, 504.1; ESI-MS 1354 (MH^+).

1.2.5. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- N -((ethoxycarbonyl)methyl)porphyrinogen 7c. δ_{H} 10.24 (br s, 1H, NH), 9.05 (s, 2H, NH), 7.65 (d, $J=2.1$ Hz, 2H, quinoid H), 7.45 (d, $J=2.2$ Hz, 2H, quinoid H), 7.42 (d, $J=2.0$ Hz, 2H, quinoid H), 7.17 (d, $J=1.9$ Hz, 2H, quinoid H), 6.74 (dd, 4H, pyrroles bearing NH), 6.69 (dd, 2H, a pyrrole bearing NH), 6.57 (s, 2H, pyrrole bearing NR), 4.26 (s, 2H, NCH_2CO_2), 3.73 (q, $J=7.1$ Hz, 2H, ethyl CH_2), 1.34 (s, 18H, *t*-butyl), 1.33 (s, 18H, *t*-butyl), 1.32 (s, 18H, *t*-butyl), 1.27 (s, 18H, *t*-butyl), 1.01 (t, $J=7.1$ Hz, 3H, ethyl CH_3); δ_{C} 186.1, 185.9 (ratio 3:1, quinoid C=O), 166.2 (COO), 149.0, 148.2, 147.3 (ratio 1:1:2, 3-quinoid), 137.2 (pyrrole (bearing NR) α -C), 135.0, 134.4, 134.1, 132.8, 132.0, 131.84 (quinoid), 131.79 (quinoid), 131.3, 130.6, 130.4, 130.3, 120.6, 120.0, 117.7, 116.3 (pyrrole β -C), 61.9 (ethyl CH_2), 46.7 (NCH_2CO_2), 35.6, 35.5, 35.3 (1:2:1, *t*-butyl quaternary C), 29.50, 29.46 (*t*-butyl CH_3), 13.8 (ethyl CH_3); UV/Vis 330.1, 511.9; ESI-MS 1212 (MH^+).

1.2.6. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- N -(*t*-butoxycarbonyl)methylporphyrinogen 7d. δ_{H} 10.44 (br s, 1H, NH), 8.91 (s, 2H, NH), 7.67 (d, $J=2.3$ Hz, 2H, quinoid H), 7.45 (hidden d, 2H, quinoid H), 7.44 (hidden d, 2H, quinoid H), 7.35 (br s, 2H,

quinoid H), 6.74 (dd, $J=7.6$ Hz, 2.2, 4H, pyrroles bearing NH), 6.65 (m, 2H, a pyrrole bearing NH), 6.54 (s, 2H, pyrrole bearing NR), 4.08 (s, 2H, NCH_2CO_2), 1.35 (s, 18H, ring *t*-butyl), 1.34 (s, 18H, ring *t*-butyl), 1.33 (s, 18H, ring *t*-butyl), 1.27 (s, 18H, ring *t*-butyl), 1.22 (s, 9H, $\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$); δ_{C} 186.2, 186.0 (quinoid C=O), 169.0 (COO), 147.3 (3-quinoid), 134.5, 133.9, 132.7, 131.8, 131.2, 130.5, 130.3, (120.8 (pyrrole β -C)), 81.8 ($\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$), 35.6, 35.5, 35.3 (1:2:1, *t*-butyl quaternary C), 29.54, 29.48, 29.3 (*t*-butyl CH_3), 28.1 ($\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$); UV/Vis 329.9, 512.7; ESI-MS 1240 (MH^+).

1.2.7. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- N_{21},N_{22},N_{23} -tri((ethoxycarbonyl)methyl)porphyrinogen 8c. Obtained in a mixture with 3c. δ_{H} 7.61 (unresolved d, 2H, quinone H), 7.50 (d, $J=2.2$ Hz, 2H, quinone H), 7.38 (s, 2H, quinone H), 7.34 (unresolved d, 2H, quinone H), 6.82 (d, $J=2.2$ Hz, 2H, pyrrole H), 6.61 (s, 2H, pyrrole H), 6.50 (s, 2H, pyrrole H), 6.44 (s, 2H, pyrrole H), 4.04–3.97 (m, 6H, CH_2 of ethyl), 3.91 (broad s, 6H, NCH_2), 1.35–1.26 (m, 72 H, *t*-Bu), 1.10–1.03 (m, 9H, CH_3 of ethyl); ESI-MS 1384 (MH^+).

1.2.8. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- N_{21},N_{22},N_{23} -tri(*t*-butoxycarbonyl)methylporphyrinogen 8d. Obtained in a mixture with 3d. δ_{H} 7.61 (d, 2H, quinoid H), 7.51 (d, 2H, quinoid H), 7.36 (overlapping signals, 4H, quinoid H), 6.83 (d, 2H, pyrrole H), 6.63 (s, 2H, pyrrole H), 6.48 (overlapping signals, 4H, pyrrole H), 3.79 (m, 6H, NCH_2), 1.57–1.22 (m, 99H, *t*-Bu); ESI-MS 1468 (MH^+).

1.2.9. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- N_{21},N_{23} -di((ethoxycarbonyl)methyl)- N_{22},N_{24} -dibenzylporphyrinogen 9. δ_{H} 7.46 (s, 4H, quinoid H), 7.25 (s, 4H, quinoid H), ~ 7.15 (m, 6H, *m*- and *p*-Ar), 6.65–6.67 (m, 12H, pyrrole H+*o*-Ar), 4.42 (s, 4H, NCH_2Ar), 4.00 (q, $J=7.0$ Hz, 4H, ethyl CH_2), 3.92 (s, 4H, NCH_2CO_2), 1.30 (s, 36H, *t*-butyl), 1.25 (s, 36H, *t*-butyl), 1.08 (t, $J=7.0$ Hz, 6H, ethyl CH_3); δ_{C} 186.1 (quinoid C=O), 167.2 (COO), 148.20, 148.17 (3-quinoid), 139.2, 138.0, 137.4, (134.5 (1-quinoid)), 131.6, 131.1 (2-quinoid), 129.7 (*meso* C), 128.7 (*m*-Ar), 128.0 (*p*-Ar), 125.9 (*o*-Ar), 120.6, 120.4 (pyrrole β -C), 61.9 (ethyl CH_2), 48.3 (NCH_2Ar), 46.6 (NCH_2CO_2), 35.5, 35.4 (*t*-butyl quaternary C), 29.4, 29.3 (*t*-butyl CH_3), 14.2 (ethyl CH_3); UV/Vis 327.9, 500.0; ESI-MS 1478 (MH^+).

1.2.10. *meso*-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)- N_{21},N_{23} -di((ethoxycarbonyl)methyl)- N_{22},N_{24} -di(*t*-butoxycarbonyl)methylporphyrinogen 10. δ_{H} 7.49–7.50 (2 overlapping d, 8H, quinoid H), 6.64 (s, 4H, pyrrole bearing $\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$), 6.63 (s, 4H, pyrrole bearing $\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$), 4.00 (q, $J=7.1$ Hz, 4H, ethyl CH_2), 3.83 (s, 4H, $\text{NCH}_2\text{CO}_2\text{Et}$), 3.69 (s, 4H, $\text{NCH}_2\text{CO}_2\text{tBu}$), 1.32 (s, 36H, ring *t*-butyl), 1.31 (s, 36H, ring *t*-butyl), 1.25 (s, 18H, $\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$), 1.07 (t, $J=7.1$ Hz, 6H, ethyl CH_3); δ_{C} 186.2 (quinoid C=O), 167.1, 166.3 (COO), 148.3, 148.2 (3-quinoid), 138.7 (pyrrole α -C), 135.1 (1-quinoid), 131.6, 131.3 (2-quinoid), 129.1, 128.7 (*meso* C), 120.05, 119.96 (pyrrole β -C), 82.8 ($\text{CH}_2\text{CO}_2\text{C}(\text{CH}_3)_3$), 61.8 (ethyl CH_2), 47.2, 46.3 (NCH_2), 35.5 (ring

t-butyl quaternary C), 29.43, 29.38 (ring *t*-butyl CH₃), 27.9 (CH₂CO₂C(CH₃)₃), 14.2 (ethyl CH₃); UV/Vis 324.9, 496.2; ESI-MS 1526 (MH⁺).

1.2.11. meso-Tetrakis-5,10,15,20-(3,5-di-*t*-butyl-4-oxa-cyclohexa-2,5-dienylene)-N₂₁,N₂₂,N₂₃-tribenzyl-N₂₄-(ethoxycarbonylmethyl)porphyrinogen 11. δ_H 7.50 (d, *J* = 2.0 Hz, 2H, quinoid H next to the pyrrole bearing CH₂CO₂CH₂CH₃), 7.31 (d, *J* = 1.9 Hz, 2H, neighboring quinoid H), 7.23 (s, 4H, quinoid H), 7.17 (m, 9H, *m*- and *p*-Ar), 6.67–6.71 (m, 14H, pyrrole H + *o*-Ar), 4.48 (s, 4H, NCH₂Ar), 4.40 (s, 2H, NCH₂Ar), 4.06 (s, 2H, NCH₂CO₂), 4.03 (q, *J* = 7.1 Hz, 2H, ethyl CH₂), 1.32 (s, 18H, *t*-butyl next to the pyrrole bearing CH₂CO₂CH₂CH₃), 1.27 (s, 18H, *t*-butyl), 1.243 (s, 18H, *t*-butyl), 1.236 (s, 18H, *t*-butyl), 1.09 (t, *J* = 7.1 Hz, 3H, ethyl CH₃); δ_C 186.1, 186.0 (quinoid C=O), 167.2 (COO), 148.1, 148.0 (3-quinoid), 139.2, 138.5, 138.4, 138.0, 137.5 (pyrrole α-C), 134.5, 133.9 (1-quinoid), 131.7 (quinoid C correlated with the H at 7.50 ppm), 131.3 (quinoid C correlated with the H at 7.23 ppm), 131.2 (quinoid C correlated with the H at 7.31 ppm), 130.5, 129.7 (*meso* C), 128.7 (*m*-Ar), 128.0 (*p*-Ar), 126.1, 126.0 (*o*-Ar), 120.8, 120.7, 120.6 (2:1:1, pyrrole β-C), 61.9 (ethyl CH₂), 48.6, 48.5 (1:2, NCH₂Ar), 46.8 (NCH₂CO₂), 35.52, 35.46, 35.4 (*t*-butyl quaternary C), 29.4, 29.31, 29.27 (1:1:2, *t*-butyl CH₃), 14.2 (ethyl CH₃); UV/Vis 328.1, 502.1; ESI-MS 1482 (MH⁺).

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